

Mechanically Strong Aerogels Formed by Templated Growth of Polymer Cross-Linkers on Inorganic Nanoparticles

In the search for materials with better mechanical, thermal, and electrical properties, it is becoming evident that oftentimes dispersing ceramic nanoparticles in plastics improves performance. Along these lines, chemical bonding (both covalent and noncovalent) between a filler and a polymer improves their compatibility, and thus enhances certain properties of the polymeric matrix above and beyond what is accomplished by simple doping with the filler. When a similarly sized dopant and matrix are used, elementary building blocks may also have certain distinct advantages (e.g., in catalysis). In this context, researchers at the NASA Glenn Research Center reasoned that in the extreme case, where the dopant and the matrix (e.g., a filler and a polymer) are not only sized similarly, but their relative amounts are comparable, the relative roles of the dopant and matrix can be reversed. Then, if the "filler," or a certain form thereof, possesses desirable properties of its own, such properties could be magnified by cross-linking with a polymer. We at Glenn have identified silica as such a filler in its lowest-density form, namely the silica aerogel.

Aerogels are used primarily in space applications as collectors of hypervelocity particles (STARDUST Program) or for thermal insulation in extreme environments (refer to the *Sojourner* Rover in 1997 or the two Mars Exploratory Rovers, *Spirit* and *Opportunity*, in 2003). For instance, it has been reported that if conventional thermal insulation had been used on the *Sojourner* Rover, 6 lb of the total 25-lb weight of the rover would have been lost for thermal insulation. Thus, it was reasoned that if the thermal insulator--the aerogel--was strong enough to comprise the building material of the entire space vehicle, more weight would be freed for useful payload.

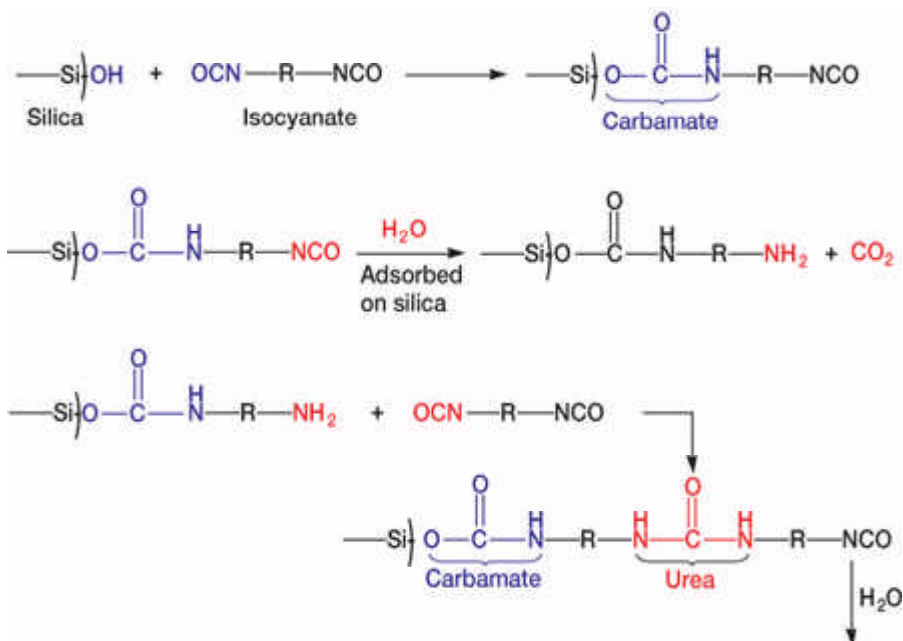
With this in mind, we were able to "glue" together the nanoparticle building blocks of a conventional silica aerogel, by templated, directed growth of the polymer on those particles. Thus, the resulting material is ~3 times more dense than the underlying silica aerogel framework but takes more than 300 times the force to break. The preceding photograph shows such a cross-linked silica aerogel monolith just before its break point.



A cross-linked silica aerogel undergoing a three-point flexural bending test. The density of the monolith is $\sim 0.55 \text{ g/cm}^3$. The density of the underlying silica is $\sim 0.18 \text{ g/cm}^3$, and the

silica has been cross-linked with polyhexamethylene diisocyanate.

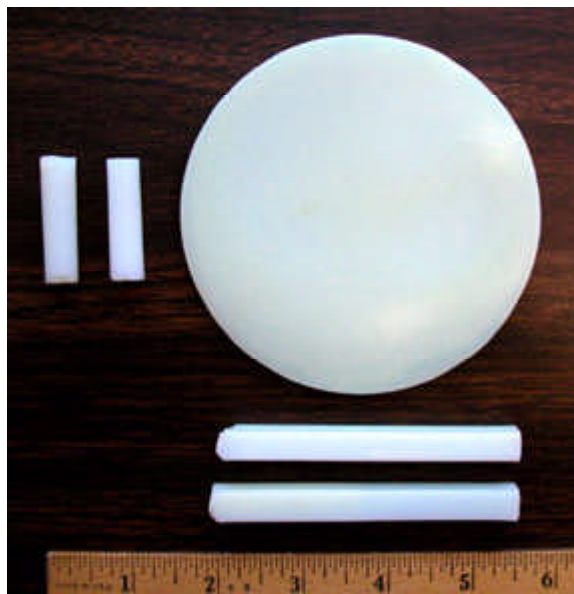
The mechanism of cross-linking has been investigated carefully, and it has been discovered that the cross-linking chemistry is based on (1) a reaction between the cross-linker and the surface of the aerogel framework and (2) a reaction of the cross-linker with itself, either via a mechanism that is catalyzed by the surface of the aerogel framework or via a reagent that is confined on that surface. Thus diisocyanates react with the surface of the aerogel, forming urethanes, or they are hydrolyzed by adsorbed water, yielding amines, which then attack other diisocyanates, forming ureas (see the chemical diagram). In addition, epoxies containing two, three, or four reactive groups undergo a ring-opening cascade of reactions with themselves as well as with amino groups that have been deliberately placed on the aerogel surface.



Cross-linking silica with a diisocyanate.

Crosslinking silica with a diisocyanate: one isocyanate reacts with the hydroxyl groups at the surface of silica to form carbamate. The free isocyanate reacts with water adsorbed on the surface of silica to form an amine and carbon dioxide as a byproduct. Then, the newly formed amine reacts with more diisocyanate leading to tethering of the nanoparticles by polyurea.

Cross-linked aerogels are strong enough to withstand the surface tension forces developing around the residing meniscus of low-vapor-pressure liquids evaporating through their bulk. So it has been found that cross-linked hydrogels can be dried to aerogels from pentane under ambient pressure, thus eliminating the need for extractions with a supercritical fluid. As a result, objects with different shapes and sizes can be produced easily.



Aerogels produced by ambient pressure drying from pentane.

Find out more about this research:

<http://www.grc.nasa.gov/WWW/MDWeb/5150/Polymers.html>

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